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The Impedance and Conductivity Studies on $BiFeO_3$ and $0.90BiFeO_3$-$0.10Bi_{0.5}Na_{0.5}TiO_3$ Ceramics

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Abstract. Polycrystalline $BiFeO_3$ and $0.90BiFeO_3$-$0.10Bi_{0.5}Na_{0.5}TiO_3$ compounds were synthesized by conventional solid state route. The compounds were crystallized in rhombohedral structure with *R3c* space group. Complex impedance studies revealed that insulating character of both grain and grain boundaries were improved in $0.90BiFeO_3$-$0.10Bi_{0.5}Na_{0.5}TiO_3$ compound. Both complex and modulus plots confirmed the presence of non- Debye type relaxations in these compounds. Frequency dependence of AC conductivity at different temperatures suggests that charge carriers follow correlated barrier hopping (CBH) model. Estimated activation energies indicated that oxygen vacancies movements are the prime contributors to the conduction in the measured temperature range.

Keywords: Multiferroics, Electrical impedance, ac conductivity, Correlated barrier hopping.
PACS: 72.20.-i.

INTRODUCTION

The simultaneous existence of the ferroelectric and (anti)ferromagnetic orders in the same phase makes the multiferroics as promising and potential candidates for practical applications in memory devices, microelectronics and spintronics.[1] $BiFeO_3$ is a room temperature multiferroic with Curie temperature T_C = 1103 K and Neel temperature T_N = 643 K. BiFeO3 generates much interest in the past few years due to its very high electrical polarizations. [2] However, in bulk form, the presence of leakage current, oxygen vacancies and antiferromagnetic nature limits its potential of $BiFeO_3$ as a material of choice for device applications. In order to resolve these drawbacks, making solid solution of BFO with perovskite based ferroelectric compounds such as $BaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$ is one of the best technique. Most of the existing reports focused on structural, magnetic and ferroelectric properties and paid less attention on electrical properties and charge carriers transport mechanism. In order to study the electrical properties, we have carried out detailed temperature and frequency dependent impedance, modulus and ac conductivity studies and observed grain, grain boundaries effects and possible charge carrier mechanism.

EXPERIMENTAL DETAILS

Conventional solid state route was used to synthesize $BiFeO_3$ (BFO) and $0.9BiFeO_3$-$0.10Bi_{0.5}Na_{0.5}TiO_3$ (BNFTO) ceramics. The detailed experimental procedure can be found elsewhere.[3] The Phase analysis of the compounds was examined by X-ray diffractometer (Panalytical X'pert Pro). Electrical properties were measured using Wayne Kerr 6500B impedance analyzer.

RESULTS AND DISCUSSIONS

Structural Studies

Rietveld refinement is carried out on the X-ray diffraction (XRD) patterns of BFO and BNFTO compounds as shown in Figure 1. From the refinement, it is revealed that the compounds are crystallized in rhombohedral structure with *R3c* (IUCr No. 161) space group. The secondary phases such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ are suppressed in BNFTO compound. Lattice parameters *a* and *c* for BFO and BNFTO compounds are respectively 5.5794 Å,

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13.8709 Å and 5.5804 Å, 13.8743 Å. The observed increased in lattice parameters and volume of the unit cell observed in BNFTO compound could be due to larger ionic size of Na^+.

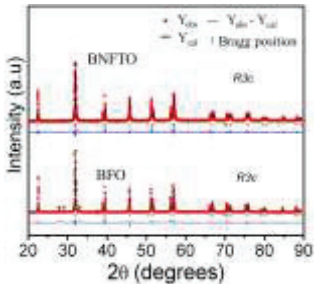

FIGURE 1. XRD patterns of BFO and BNFTO compounds. • and ∗ represent impurity phases corresponding to $Bi_{25}FeO_{40}$ and $Bi_2Fe_4O_9$ respectively.

Impedance Studies

Frequency variation of real part of impedance (Z') for BFO and BNFTO are shown in Figure 2. Negative temperature coefficient of resistance (NTCR) character is evident from temperature dependent Z'. Increase in Z' value in BNFTO compound, at any temperature compared to BFO, suggests that an enhancement of the bulk resistance of the compounds which could be due to the reduction of oxygen vacancies.

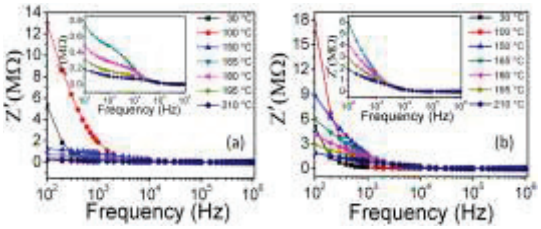

FIGURE 2. Frequency variation of real part of impedance (Z') for (a) BFO and (b) BNFTO compounds. Insert shows the enlarged view above 150 °C.

The grain and grain boundary contributions to the electrical resistivity can be extracted by fitting the impedance data (Z' vs Z'') using two RC parallel circuit model whose resultant impedance in terms of grain and grain boundary resistances (R) and capacitances (C) is given as

$$Z^* = \frac{R_g}{1+(j\omega R_g C_g)^{n_g}} + \frac{R_{gb}}{1+(j\omega R_{gb} C_{gb})^{n_{gb}}} \quad (1)$$

where n is the relaxation time distribution function and is a measure of deviation from ideal Debye behavior. As there are two semicircular arcs appear in Nyquist plot from 150 °C to 225 °C, the values of grain boundary resistance R_{gb} and grain resistance R_g are estimated by fitting the Nyquist plots. A typical Nyquist plots for BFO and BNFTO compounds at 210 °C are shown in Figure 3. With the increase of temperature from 150°C to 225°C, the values of R_{gb} and R_g decrease respectively from 8.4 MΩ to 1MΩ and 0.9 MΩ to 42 kΩ for BFO and 32.6 MΩ to 2.02 MΩ and 6.15 MΩ to 0.37 MΩ for BNFTO compounds. The appearance of depressed semicircular arc indicates presence of non-Debye type relaxations.

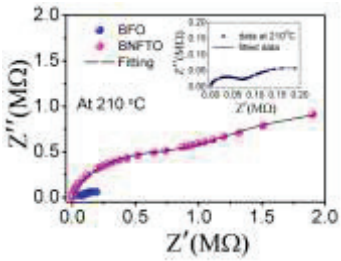

FIGURE 3. Nyquist plots for BFO and BNFTO compounds at 210 °C. Inset show enlarged view of Nyquist plot for BFO.

The dc conductivity σ_{dc} of the compounds corresponding to grain (or grain boundary) are calculated from the equation,

$$\sigma_{dc} = \frac{d}{AR} \quad (2)$$

where d is the thickness of the compound, R is the grain (or grain boundary) resistance of the compound and A is the area of the electrode. Both grain and grain boundary dc conductivities and grain relaxation time τ_g (= R_gC_g) are thermally activated and follow Arrhenius equation as given below

$$A = A_o e^{-E/kT} \quad (3)$$

Activation energies calculated from equation 3 for grain and grain boundary and grain relaxation times are respectively designated as E_{dg}, E_{dgb} and E_g and are given in Table. 1. The activation energies clearly indicate that short range movement of oxygen ion vacancies will be responsible for the conduction in the compounds between150 °C to 225 °C.

Impedance Studies

The electric modulus (M^*) is expressed in terms of impedance as

$$M^* = M' + iM'' = i\omega C_o Z^* \quad (4)$$

where ω is the frequency and C_o is the capacitance in vacuum. Frequency variation of imaginary part of electric modulus (M'') at different temperatures for BFO and BNFTO compounds are shown in Figure 4. M'' shows a peak (M''_{max}) at a particular frequency which shifts towards higher frequency side with the temperature. The frequency (ω_{max}) corresponding to M''_{max} follows Arrhenius law,

$$\omega_{max} = \omega_o e^{-E_M/kT} \quad (5)$$

where ω_o is the pre-exponential factor and E_M is the activation energy. The activation energies are extracted from the equation 5 and are given in Table. 1. Further, the broadening of peaks indicates the presence of non-Debye type relaxations in these compounds.

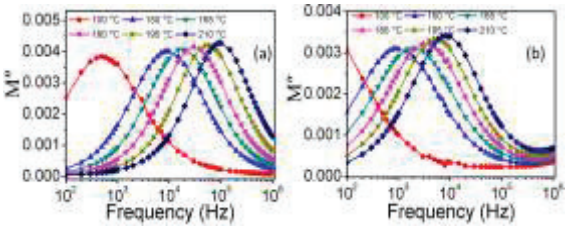

FIGURE 4. Frequency variation of imaginary part of electric modulus (M'') for (a) BFO and (b) BNFTO compounds.

ac Conductivity Studies

The frequency dependence of ac conductivity at different temperatures is shown in Figure 5. The frequency dependence of ac conductivity obeys Joncher's power law

$$\sigma_{a.c} = \sigma(0) + A\omega^s \quad (6)$$

where $\sigma(0)$ is the dc conductivity and s is an exponent. At a given temperature, ac conductivity is significantly reduced in BNFTO compound due to the reduction in oxygen vacancies.

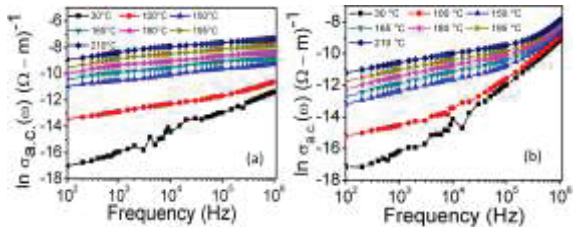

FIGURE 5. The frequency dependence of ac conductivity for (a) BFO and (b) BNFTO compounds.

The frequency dependence part $\sigma(\omega)$ is consistent with the correlated barrier hopping (CBH) model.[4]

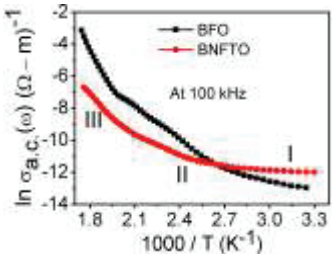

FIGURE 6. Temperature dependence of ac conductivity for BFO and BNFTO compounds.

Figure 6 shows the Arrhenius plots of ac conductivity at 100 kHz for BFO and BNFTO compounds. The temperature dependence of ac conductivity can be represented by the Arrhenius equation

$$\sigma_{a.c} = \sigma_o \exp(-E/kT) \quad (7)$$

where σ_o is the electric conductivity. The activation energies are calculated at 100 kHz for BFO and BNFTO compounds are given in Table 1. In region I (below 393K), conductivity is attributed to the electronic hopping. In region II (393K – 503K), conductivity is due to short range movement of oxygen vacancies. In region III (503K – 573K), conductivity is attributed to long range movement of oxygen vacancies or creation of defects.[5]

TABLE 1. Activation energies of BFO and BNFTO compounds estimated from different formalisms.

Comp-ound	Activation energies (eV)						
	E_g	E_{dg}	E_{dgb}	E_M	$E_{\sigma 1}$	$E_{\sigma 2}$	$E_{\sigma 3}$
BFO	0.68	0.76	1.00	0.69	0.18	0.59	1.38
BNFTO	0.59	0.65	0.84	0.67	0.06	0.36	0.89

CONCLUSIONS

The polycrystalline $BiFeO_3$ and $0.90BiFeO_3$-$0.10Bi_{0.5}Na_{0.5}TiO_3$ ceramics were synthesized by conventional solid-state route. Complex impedance studies revealed that insulating character was improved and ac conductivity is reduced in $0.90BiFeO_3$-$0.10Bi_{0.5}Na_{0.5}TiO_3$ compound due to the reduction in oxygen vacancies. The temperature dependence of ac conductivity indicated that charge carriers follow correlated barrier hopping model and oxygen vacancy movements are the prime contributors to the conductivity.

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